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Transition Metal and Rare Earth Compounds

Excited States, Transitions, Interactions II

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Volume Editor: Hartmut Yersin

With contributions by
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Preface

For a long time, the properties of transition metal and rare earth compounds have fascinated chemists and physicists from a scientific view-point. More recently, their enormous potential as new materials has also been explored. Applications in different fields have already been realized or are under current investigation, e.g. new laser materials, IR to visible upconversion materials, systems involving photoredox processes for solar energy conversion, new photovoltaic devices, chemical sensors, biosensors, electroluminescent devices (OLEDs) for flat panel display systems, supramolecular devices with wide-range definable photophysical properties, materials for energy harvesting, optical information and storage systems, etc. Metal complexes are also highly important in biology and medicine. Most of the applications mentioned are directly related to the properties of the electronic ground state and the lower-lying excited states. Metal complexes with organic ligands or organometallic compounds exhibit outstanding features as compared to purely organic molecules. For instance, metal compounds can often be prepared and applied in different oxidation states. Furthermore, various types of low-lying electronic excitations can be induced by a suitable choice of the metal center and/or the ligands, such as metal-centered (MC, e.g. d-d* or f-f* transitions), ligand-centered (LC, e.g. π-π*), metal-to-ligand-charge transfer (MLCT, e.g. d-π*), intra-ligand-charge-transfer (ILCT) transitions, etc. In particular, the orbitals involved in the resulting lowest excited states determine the photophysical and photochemical properties and thus the specific use of the compound. It is also of high interest that the lowest excited electronic states can be shifted over the large energy range from the U.V. to the I.R. by chemical variation of the ligands and/or the central metal ion. Moreover, these excited states have mostly spin-multiplicities different from those of the electronic ground states. Thus, in contrast to organic molecules, spin-orbit coupling (induced by the metal center) is of crucial importance, for example, for the splitting and the population and decay dynamics of these multiplets as well as for transition probabilities and radiative deactivation paths. In summary, transition metal and rare earth compounds can be prepared with photophysical properties that are over wide ranges user-definable.

In view of the fascinating potential of these compounds, it is of substantial interest to develop a deeper understanding of their photophysical properties. In this volume [1], leading scientists present modern research trends in comprehen-

[1] See also the preceding volumes, Electronic and Vibronic Spectra of Transition Metal Complexes I and II, edited by H. Yersin, Topics in Current Chemistry 171 (1994) and 191 (1997).

sive reviews which not only provide a deep insight into the specific subjects, but are also written in a style that enables researchers from related fields and graduate students to follow the interesting presentations. In particular, in the present volume Daniel R. Gamelin and Hans U. Güdel review upconversion processes in luminescent transition metal and rare earth systems. Mark J. Riley relates geometric and electronic properties of copper(II) compounds. Finally, Hartmut Yersin and Dirk Donges discuss on the basis of case studies photophysical properties of organometallic and related compounds and demonstrate how these properties can be tuned by chemical variation. In a companion volume (Topics in Current Chemistry 213), Kevin L. Bray presents effects that are observed under application of high pressure. Max Glasbeek introduces us to optically detected magnetic resonance (ODMR) techniques as applied to transition metal complexes and Arnd Vogler and Horst Kunkely give a summary concerning the diversity of excited states as found in various compounds.

I hope that the contributions in the present and in the companion volume demonstrate the attractiveness and the enormous potential of metal compounds and that a more detailed understanding of the photophysical properties will open pathways for new developments.

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Hartmut Yersin

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Upconversion Processes in Transition Metal and Rare Earth Metal Systems

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The design and characterization of new luminescent materials is an active area of research. Here we present several current topics in the area of upconversion by transition-metal and rare-earth-metal doped halide lattices. Following introduction to the necessary background material related to upconversion mechanisms and kinetics, a series of topics are discussed which illustrate some key areas of developing interest in the field. These include the use of unconventional experimental and theoretical techniques for gaining insight into upconversion processes in rare-earth-doped lattices (e.g., power-dependence measurements, two-color laser excitation schemes, and correlated crystal field calculations), as well as several specific examples of exciting and unusual upconversion behavior in both transition-metal and rare-earth-metal systems. Finally, we discuss the variety of interesting effects host-lattice variation can have on the upconversion processes of a dopant ion, ranging from multiphonon relaxation properties to exchange interactions.

Keywords: Upconversion, Luminescence, Transition metals, Rare-earth metals, Doped halide lattices

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1 Introduction

Luminescent materials play an important role in many technologies, including display screens, optical communication amplifiers, lamps, and solid-state lasers. To this end, a tremendous volume of fundamental research has been devoted to the design and characterization of new luminescent materials displaying novel photophysical effects. Among such application-oriented research, a great deal of attention has been given to the development of materials capable of generating short-wavelength radiation from long-wavelength pump sources. Second-harmonic generation (SHG) [1], simultaneous two-photon absorption (STPA) [2], and upconversion (UC) [3–6], illustrated in Fig. 1, are three well-established methods for performing this conversion. Briefly, SHG generates new frequencies through the weakly wavelength-dependent hyperpolarizability of a substance, and requires intense coherent excitation sources. STPA involves the excitation of luminescence from a real excited state at shorter wavelength than the excitation photons, and is achieved through a small but non-zero absorption cross section at the pump wavelength. Finally, upconversion generates shorter wavelength luminescence through sequential discrete absorption and/or energy-transfer steps involving real metastable excited states of the chromophore. Upconversion thus relies on the presence of multiple metastable excited states, and this leads to dramatically different photophysical properties relative to the former two methods.

In this article, we discuss several specific topics of current interest in the area of upconversion involving metal ions doped into well-known halide host lattices. Rather than attempting to provide a complete historical survey, the emphasis is on identifying developing areas of research. These range from experimental and calculational approaches for studying general upconversion processes to the investigation of new classes of upconversion materials. In the latter area, the principle strategies for obtaining new upconversion materials involve (1) variation of the host lattice and (2) variation of the dopant metal ions. Variation of the host lattice, for example, from one having high phonon energies (e.g., fluo-

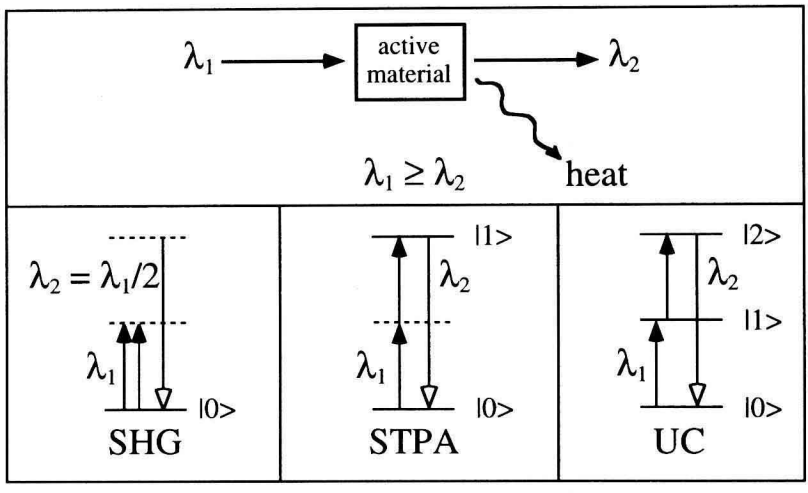

Fig. 1. Schematic representation of three common nonlinear processes that convert low-energy photon pump sources into higher-energy output: SHG = Second Harmonic Generation, STPA = Simultaneous Two-Photon Absorption, UC = Upconversion. Adapted from [17]

ride, oxide) to one having low phonon energies (e.g., chloride, bromide, iodide), can dramatically affect the competition between multiphonon and other radiative and nonradiative processes, and may lead to entirely different upconversion luminescence properties of a given ion. The use of host materials with specific optical or magnetic properties may also influence the upconversion properties of a dopant ion through sensitization or perturbation by exchange interactions. A change in metal ions can of course also have a dramatic effect. Here, we relate examples that emphasize the relatively unexplored upconversion properties of transition metals. When compared to the rare-earth ions, which by far dominate the upconversion literature, transition metals can be expected to show a number of differences in the relevant parameters that govern the upconversion dynamics. In particular, the larger radial extension of the d-orbitals than of the f-orbitals may lead to larger electron-phonon coupling strengths and a greater susceptibility to crystal-field and exchange perturbations. Finally, the design and study of new chromophores comprised of combinations of metal ions is emphasized. Here we present a few examples from our research with these new materials that show unusual upconversion properties attributable to exchange interactions between metal ions. In these examples, including rare-earth/rare-earth, rare-earth/transition-metal, and transition-metal/transition-metal ion pairs, exchange interactions are found to be particularly important when the ions are situated in close proximity to one another by the geometric constraints of the host material. The options available in the choice of hosts and codopant combinations can cover a very broad range of possibilities, leaving much to the imagination and creativity of the researcher, and illustrating the ability to use well-founded chemical principles to design and construct upconversion materials displaying exciting new photophysical properties.

2 Excited-State Decay

The minimum prerequisite for generation of upconversion luminescence by any material is the presence of at least two metastable excited states. In order for upconversion to be efficient, these states must have lifetimes sufficiently long for ions to participate in either luminescence or other photophysical processes with reasonably high probabilities, as opposed to relaxing through nonradiative multiphonon pathways. The observed decay of an excited state in the simplest case scenario, as probed for example by monitoring its luminescence intensity I, behaves as an exponential:

$$I(t) = I(0)\, e^{-k_{tot}t} \tag{1}$$

where the observed decay rate constant, k_{tot}, derives from the sum of all contributing radiative (rad) and nonradiative (nr) decay processes:

$$k_{tot} = k_{rad} + k_{nr} = \tau_{obs}^{-1} \tag{2}$$

Among the possible nonradiative processes, multiphonon relaxation generally makes the greatest contribution to k_{tot}. Multiphonon relaxation is most easily illustrated within the framework of the single configurational coordinate (SCC) model [7,8]. This model assumes that the vibrational wavefunction overlap integrals responsible for multiphonon relaxation can be approximated by the interactions between the donor (excited) and acceptor (e.g., ground state) potential surfaces along one single effective nuclear coordinate, Q_{eff}. In cases where excited-state nuclear distortions are small, assuming harmonic potentials, identical ground- and excited-state force constants, and identical normal-coordinate descriptions, the SCC model describes the $T = 0$ K multiphonon decay rate constant as shown in Eq. (3):

$$k_{mp}(0) \approx (C)\left(\frac{e^{-S}S^p}{p!}\right) \tag{3}$$

Here, $p = \Delta E_{0-0}/\nu_{eff}$ is the dimensionless energy gap between the upper state and the closest lower-energy state in units of the effective vibrational energy, $\nu_{eff}\,(cm^{-1})$. C is the electronic factor, and S is the Huang-Rhys dimensionless excited-state distortion parameter in units of vibrational quanta ν_{eff}. As shown in Eq. (2), k_{mp} is strongly dependent on p. Additionally, for a given reduced energy gap p, the introduction of even small excited-state distortions, S, can rapidly enhance the radiationless multiphonon relaxation rate such that this dominates the total 0 K relaxation. This model is easily extended to elevated temperatures, where substantial increases in k_{mp} may be observed [7,8].

For the case of only one radiative decay channel, the radiative decay rate constant in Eq. (2) is described by Eq. (4) [9], where n is the index of refraction, the constant $\alpha = 1.5 \times 10^4\ s/m^2$, and g denotes the degeneracy of the ground (a) or excited (b) state involved in the transition:

$$k_{rad} = f\frac{g_a}{g_b}\frac{n[(n^2+2)/3]^2}{\alpha\lambda^2} \quad (4)$$

The radiative rate constant is thus directly proportional to the oscillator strength, f, of the transition, and is influenced by both degeneracies and the transition wavelength.

The vast majority of luminescent systems have only one emitting excited state, typically the lowest excited state [10]. This is because nonradiative relaxation tends to be extremely rapid among excited states due to the presence of high-frequency vibrations (e.g., stretching vibrations involving protons), small inter-excited-state energy gaps, and sizable electron-phonon coupling strengths. This situation is contrasted by the behavior of the rare-earth metal ions in crystals or complexes. Due to the high shielding of their *f* electrons, rare-earth ions are characterized by an extreme insensitivity to their environment, in particular having very small electron-phonon coupling strengths, S, in their various f-f excited states. As a result, k_{mp} values can be quite small, and many rare earth excited states are found to luminesce if separated from the nearest lower excited state by only ca. 6 quanta of the highest frequency vibration. Rare-earth ions therefore often have a series of luminescent f-f excited states, a property which makes them suitable for use in upconversion materials.

Since the first observations of upconversion in the mid-1960s [11–14], hundreds of studies involving most of the lanthanide and many actinide ions have been reported [3–5]. In many cases, efficient two-, three-, or four-quantum upconversion is observed. Recent milestones include the development of several all-solid-state rare-earth upconversion lasers operable at room temperature [6, 15], and the demonstration of a viable three-dimensional imaging technique based on rare-earth upconversion [16]. More recently, several transition-metal materials have also been shown to display interesting upconversion properties [17]. In these transition-metal systems a greater range of ground and excited state properties is observed, including stronger electron-phonon coupling strengths in some cases, and this may lead to new, unprecedented upconversion properties (Sects. 11 and 12).

3 The Building Blocks of Upconversion: Absorption and Energy Transfer

A wide variety of upconversion mechanisms have been proposed and observed. The majority of these involve some combination of absorption and nonradiative energy-transfer (ET) steps. Absorption may come in two basic forms. Ground-state absorption (GSA, Fig. 2a) results in promotion of an ion from its ground state to an excited state. Excited-state absorption (ESA, Fig. 2b) involves absorption of a photon by an excited ion, and results in promotion of that ion to a higher excited state.

The simplest upconversion mechanism possible is therefore that of GSA followed by ESA (GSA/ESA). GSA/ESA upconversion is inherently a single-chromophore effect, and as a consequence this mechanism is relatively insensitive to

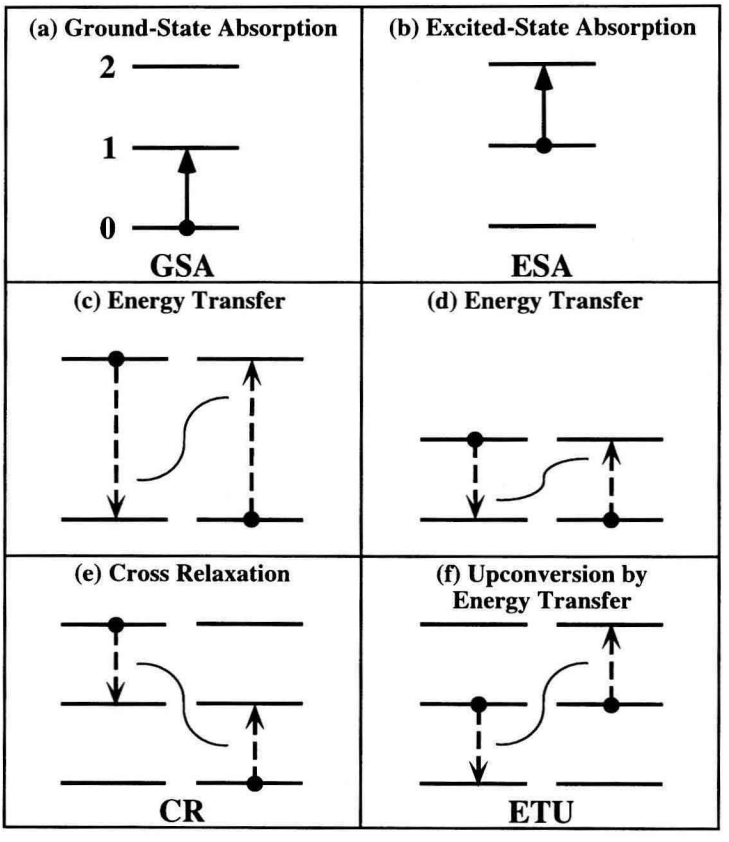

Fig. 2a–f. The basic building blocks of upconversion, and related processes. *Solid arrows* indicate radiative processes, and *dashed arrows* indicate nonradiative processes

concentration of the upconversion ion. For absorption over a sample length, l, that is short compared to the absorption length, the absorption pump rate $R_{a,b}$(ions/cm^{3}s) for a transition $a \rightarrow b$ is given by

$$R_{a,b} = \frac{\lambda_p}{hc\pi w_p^2} P \sigma_a N_a \tag{5}$$

where P(W/cm^2) is the incident pump power, λ_p is the pump wavelength, w_p is the pump radius, h is Planck's constant, c is the vacuum speed of light, σ_a is the absorption cross section from level a to level b, and N_a (ions/cm^3) is the population density of level a. In a three-level system, the rate constant for a GSA process between levels 0 and 1 is defined as $G = R_{0,1}/N_0$, and that for an ESA process between levels 1 and 2 is defined as $E = R_{1,2}/N_1$. For the GSA/ESA upconversion process to occur, both R_{GSA} ($R_{0,1}$) and R_{ESA} ($R_{1,2}$) must be nonzero. In the simple three-level scheme shown in Fig. 2a, b, at low pump rates, the population of

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